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(56) Documents Cited

**US 4624968 A**  
**Chemical Abstract No 131:353528 & CN 1137078**  
**(B.ZHONG ET AL)**

(58) Field of Search

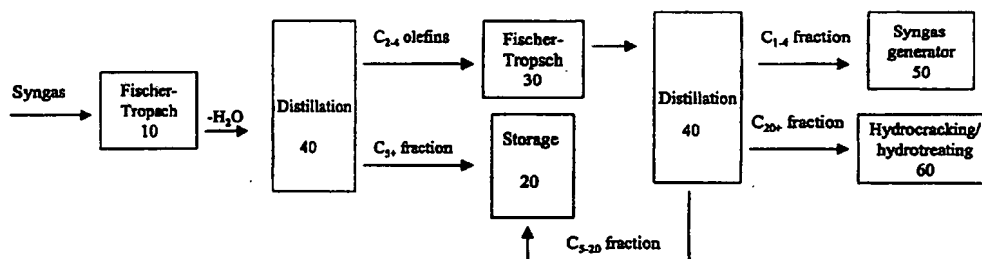
**UK CL (Edition S) C5G GAD**  
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(54) Abstract Title

**Multi stage Fischer-Tropsch process for the synthetic preparation of liquid fuels**

(57) An integrated process for producing liquid fuels from syngas via a two-stage Fischer-Tropsch reaction is disclosed. The first stage of the Fischer-Tropsch chemistry is performed using conditions in which chain growth probabilities are relatively low to moderate, and the product of the reaction includes a relatively high proportion of low molecular ( $C_{2-8}$ ) weight olefins and a relatively low proportion of high molecular weight ( $C_{30+}$ ) waxes. The product from the first stage is fed into the second stage where the chain growth probabilities are relatively high. The wax and other paraffins produced in the first reaction are largely inert under these conditions. The light olefins compete with heavier olefins for chain initiation, and fewer chains will be initiated at  $C_{20+}$ . With most chains initiated at  $C_{2-8}$ , moderate chain growth probability will produce a relatively larger fraction in the  $C_{5-12}$  range. In this manner, wax yield is minimized.

FIGURE 4



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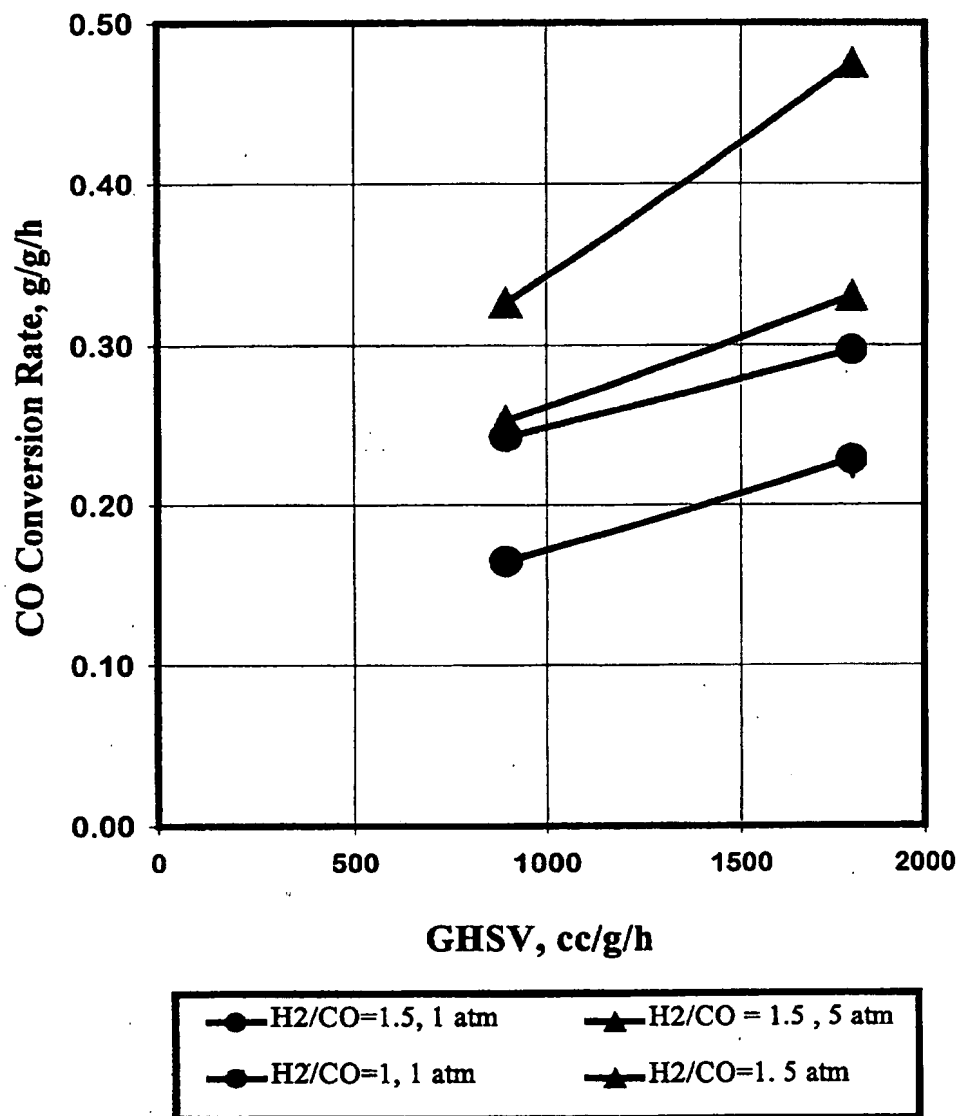
**Figure 1. CO Conversion vs GHSV**

Figure 2. Synthesis Rates 1 atm, 200°C, 1800 cc/g/h

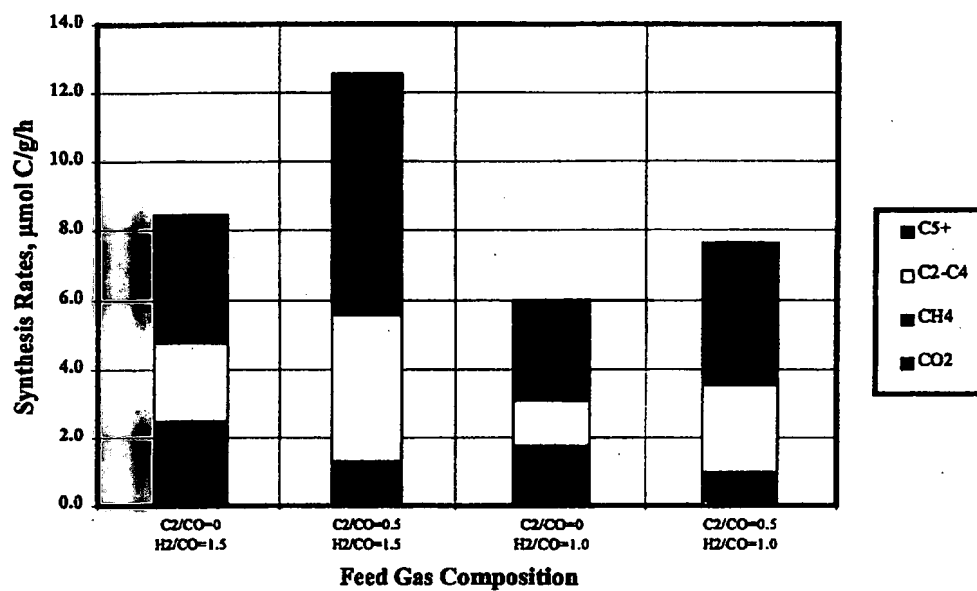


Figure 3. Synthesis Rates 5 atm, 200°C, 1800 cc/g/h

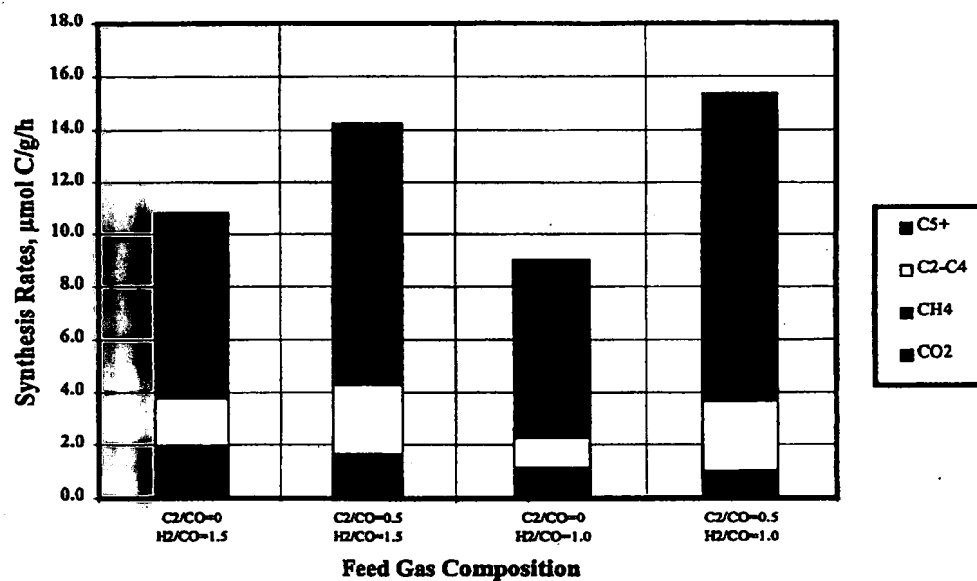
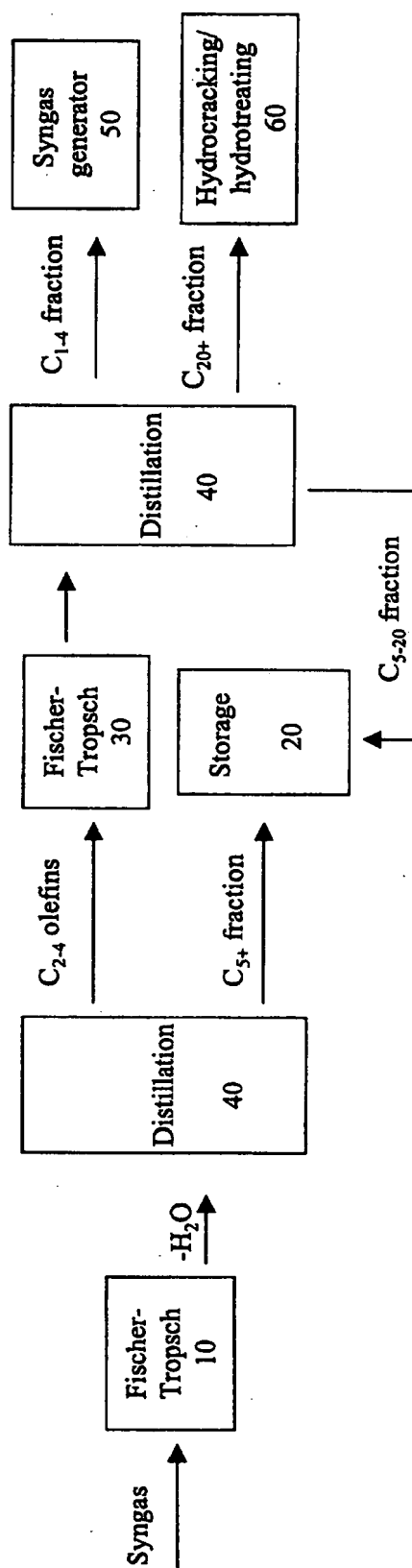


FIGURE 4



1 INCREASED LIQUID SENSITIVITY DURING FISCHER-TROPSCH  
2 SYNTHESIS BY OLEFIN INCORPORATION

3  
4 BACKGROUND OF THE INVENTION

5  
6 The majority of combustible fuel used in the world today is derived from crude  
7 oil. There are several limitations to using crude oil as a fuel source. Crude oil  
8 is in limited supply; it includes aromatic compounds believed to cause cancer,  
9 and contains sulfur and nitrogen-containing compounds that can adversely  
10 affect the environment, for example, by producing acid rain.

11  
12 Combustible liquid fuels can also be prepared from natural gas. This involves  
13 converting the natural gas, which is mostly methane, to synthesis gas, or  
14 syngas, which is a mixture of carbon monoxide and hydrogen. An advantage  
15 of using fuels prepared from syngas is that they do not contain nitrogen and  
16 sulfur and generally do not contain aromatic compounds. Accordingly, they  
17 have minimal health and environmental impact. \*

18  
19 Fischer-Tropsch chemistry is typically used to convert the syngas to a product  
20 stream that includes combustible fuel, among other products. A limitation  
21 associated with Fischer-Tropsch chemistry is that it tends to produce a broad  
22 spectrum of products, ranging from methane to wax. Product slates for  
23 syngas conversion over Fischer-Tropsch catalysts (Fe, Co and Ru) are  
24 controlled by polymerization kinetics with fairly constant chain growth  
25 probabilities, which fix the possible product distributions. Heavy products with  
26 a relatively high wax content are produced when chain growth probabilities  
27 are high. Methane is produced with high selectivity when chain growth  
28 probabilities are low.

29  
30 Methane can be recirculated to ultimately yield combustible liquid fuel. Wax  
31 can be processed, for example, by hydrocracking and/or hydrotreating  
32 followed by oligomerization, to yield combustible liquid fuel. However, it would

1 be advantageous to have new methods for providing a product stream from a  
2 Fischer-Tropsch process that has a higher proportion of combustible liquid  
3 fuel with less methane to recirculate and less wax to process.

4  
5 One method used in the past to minimize methane production has been to  
6 incorporate olefins in the Fischer-Tropsch reaction. Work in the early 1930's  
7 used a roughly 1:1 ratio of hydrogen/carbon monoxide, and added olefins to  
8 the reaction mixture (Smith et al., J.A.C.S., 52:3221 (1930). This tended to  
9 provide oxygenated material, which is not preferred. U.S. Patent  
10 No. 4,754,092 to Iglesia et al. discloses incorporating olefins into a  
11 Fischer-Tropsch reaction, but does not specify the type of chain growth  
12 probabilities for the reaction, and discloses using a wide range of  
13 hydrogen/carbon monoxide ratios such that it would be difficult to predict  
14 whether the product would be oxygenated, olefinic, or saturated.

15  
16 It would be advantageous to provide methods for improving product yields in  
17 Fischer-Tropsch reactions, while minimizing methane and oxygenate  
18 production. The present invention provides such methods.

19  
20 SUMMARY OF THE INVENTION

21  
22 In its broadest aspect, the present invention is directed to an integrated  
23 process for producing liquid fuels from syngas via a two-stage  
24 Fischer-Tropsch reaction. The first stage of the Fischer-Tropsch chemistry is  
25 performed using conditions in which chain growth probabilities are relatively  
26 low to moderate, and the product of the reaction includes a relatively high  
27 proportion of low molecular ( $C_{2-8}$ ) weight olefins and a relatively low proportion  
28 of high molecular weight ( $C_{30+}$ ) waxes.

29  
30 The products of the first stage include methane,  $C_{2-4}$  hydrocarbons,  $C_5+$   
31 hydrocarbons, water and carbon dioxide, as well as unreacted syngas.  
32 Optionally, but preferably, water produced in the first stage is substantially

1 removed before the product stream is sent to the second stage. Optionally,  
2 the product is hydrotreated at this stage to remove any oxygenated products.  
3 Further,  $C_5+$  hydrocarbons are preferably isolated. In one embodiment, at  
4 least a portion of the olefins is isomerized prior to being fed into the second  
5 stage.

6  
7 The product from the first stage, after any optionally performed processing  
8 steps, is then fed into the second stage where the chain growth probabilities  
9 are relatively high. The wax and other paraffins produced in the first reaction  
10 are largely inert under these conditions. The light olefins compete with  
11 heavier olefins for chain initiation, and fewer chains will be initiated at  $C_{20+}$ .  
12 With most chains initiated at  $C_{2-8}$ , moderate chain growth probability will  
13 produce a relatively larger fraction in the  $C_{5-12}$  range. In this manner, wax  
14 yield is minimized.

15  
16 The syngas used in both stages preferably contains certain ratios of hydrogen  
17 to carbon monoxide. In the first stage, hydrogen/carbon monoxide ratios in  
18 excess of about 1.0/1.0 tend to provide less olefins and more hydrogenated  
19 products, although changing the temperature and/or pressure may mitigate  
20 these effects to some degree. In the second stage, using a cobalt-containing  
21 catalyst, a ratio of hydrogen to carbon monoxide greater than 1.5/1.0 tends to  
22 provide a product that is greater than 80% saturated. At a ratio of about  
23 1.0/1.0, the product tends to include oxygenates and olefins.

24  
25 In one embodiment, the Fischer-Tropsch synthesis with low to moderate chain  
26 growth probability is performed using an iron-containing catalyst in the first  
27 reactor, and Fischer-Tropsch synthesis with high chain growth probability is  
28 performed using a cobalt-containing catalyst in the second reactor.

29



BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph comparing the CO conversion (%) vs gas hourly space velocity (GHSV) for the reaction in Example 1.

Figure 2 is a graph comparing the synthesis rates ( $\mu\text{mol C/g/h}$ ) vs feed gas composition for those experiments in Example 1 run at a pressure of 1 atm, a temperature of  $200^{\circ}\text{C}$ , and a GHSV of  $1800\text{ cc/g/h}$ . The dark portion of the bar represents the  $\text{C}_5+$  fraction. The white portion of the bar represents the  $\text{C}_{2-4}$  fraction. The gray portion of the bar represents the  $\text{CH}_4$  fraction. The gray portion of the bar with diagonal lines through it represents the  $\text{CO}_2$  fraction.

Figure 3 is a graph comparing the synthesis rates ( $\mu\text{mol C/g/h}$ ) vs feed gas composition for those experiments in Example 1 run at a pressure of 5 atm, a temperature of  $200^{\circ}\text{C}$ , and a GHSV of  $1800\text{ cc/g/h}$ . The dark portion of the bar represents the  $\text{C}_5+$  fraction. The white portion of the bar represents the  $\text{C}_{2-4}$  fraction. The gray portion of the bar represents the  $\text{CH}_4$  fraction. The gray portion of the bar with diagonal lines through it represents the  $\text{CO}_2$  fraction.

Figure 4 is a schematic flow diagram representing one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to an integrated process for producing liquid fuels from syngas. As used herein, the term "integrated process" refers to a process comprising a sequence of steps, some of which may be parallel to other steps in the process, but which are interrelated or somehow dependent upon either earlier or later steps in the total process.

1 In Fischer-Tropsch chemistry, products with a relatively high molecular weight  
2 and with a relatively high selectivity for wax are produced when chain growth  
3 probabilities are high. Methane and lower molecular weight products,  
4 including a variety of low molecular weight ( $C_{2-8}$ ) olefins, are produced with  
5 high selectivity when chain growth probabilities are low.

6

7 The process described herein includes a two stage Fischer-Tropsch reaction.  
8 The first stage of the Fischer-Tropsch chemistry is performed using conditions  
9 in which chain growth probabilities are relatively low to moderate, and the  
10 product of the reaction includes a relatively high proportion of low molecular  
11 ( $C_{2-8}$ ) weight olefins and a relatively low proportion of high molecular weight  
12 ( $C_{30+}$ ) waxes. For example, catalysts with low alpha values, i.e., between  
13 about 0.600 and 0.700, provide a relatively high proportion of low molecular  
14 weight olefins and a relatively low amount of wax, i.e., less than about 10% by  
15 weight. Catalysts with moderate alpha values, i.e., between 0.700 and 0.800,  
16 provide a moderate proportion of low molecular weight olefins and a moderate  
17 amount of wax, i.e., between about 2 and 10% by weight.

18

19 The products of this reaction are fed into the second stage where the chain  
20 growth probabilities are relatively high, for example, using catalysts with an  
21 alpha value above about 0.800, and preferably, above about 0.850. As a  
22 general rule, as the alpha value of the catalyst increases, the amount of  
23 methane production decreases.

24

25 Paraffins produced in the first reaction are largely inert under these  
26 conditions. The low molecular weight ( $C_{2-8}$ , preferably  $C_{2-4}$ ) olefins compete  
27 with heavier molecular weight olefins for chain initiation, and fewer chains are  
28 initiated at  $C_{20+}$  than if syngas alone is used as feed for a Fischer-Tropsch  
29 reaction using the same catalyst.

30

31 Using the process described herein, most chains in the second stage of the  
32 Fischer-Tropsch process are initiated at  $C_{2-8}$ , resulting in moderate chain

1 growth probability which produces a relatively larger fraction in the C<sub>5-12</sub>  
2 range. In this manner, wax yield is minimized. One of the benefits of  
3 performing the two-stage Fischer-Tropsch reaction is that the use of a  
4 hydrocracker can be minimized or, ideally, eliminated altogether.

5  
6 While not wishing to be bound to a particular theory, the presence of ethylene  
7 and other lower molecular weight olefins in the feed to the second reactor is  
8 believed to compete with higher olefins. This provides a product with an  
9 overall lower average molecular weight than if the reaction is done in the  
10 absence of added olefins. Ethylene, in particular, is unhindered at both ends,  
11 and therefore has twice the probability of starting a chain than an olefin  
12 hindered at one end. Larger molecular weight olefins, while resting on the  
13 catalyst bed, can either be hydrogenated to form paraffinic products that are  
14 largely inert, or can compete with the smaller olefins to be incorporated into  
15 the growing chain. What is generally observed is that the large olefins tend to  
16 be hydrogenated rather than being incorporated into the growing chain.

#### 17 Fischer-Tropsch Chemistry

18  
19 In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by  
20 contact with a Fischer-Tropsch catalyst under reactive conditions. Depending  
21 on the quality of the syngas, it may be desirable to purify the syngas prior to  
22 the Fischer-Tropsch reactor to remove carbon dioxide produced during the  
23 syngas reaction and any sulfur compounds, if they have not already been  
24 removed. This can be accomplished, for example, by contacting the syngas  
25 with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a  
26 packed column.

27  
28 Examples of conditions for performing Fischer-Tropsch type reactions are well  
29 known to those of skill in the art. Suitable conditions are described, for  
30 example, in U.S. Patent Nos. 4,704,487, 4,507,517, 4,599,474, 4,704,493,

1 4,709,108, 4,734,537, 4,814,533, 4,814,534 and 4,814,538, the contents of  
2 each of which are hereby incorporated by reference in their entirety.

3  
4 In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on  
5 a metal oxide support. The catalysts may also contain a noble metal  
6 promoter(s) and/or crystalline molecular sieves. Certain catalysts are known  
7 to provide chain growth probabilities that are relatively low to moderate, and  
8 the product of the reaction includes a relatively high proportion of low  
9 molecular ( $C_{2-8}$ ) weight olefins and a relatively low proportion of high  
10 molecular weight ( $C_{30+}$ ) waxes. Certain other catalysts are known to provide  
11 relatively high chain growth probabilities. Such catalysts are well known to  
12 those of skill in the art and can be readily obtained and/or prepared.

#### 13 14 Catalyst Selection

##### 15 Catalysts with low chain growth probabilities

16  
17 For the first stage of the Fischer-Tropsch reaction, any catalyst that provides  
18 relatively low to moderate chain growth probabilities can be used. Typically,  
19 catalysts with an alpha value between about 0.600 and 0.700 provide low  
20 chain growth probabilities. Catalysts with an alpha value between about  
21 0.700 and 0.800 provide moderate chain growth probabilities. Preferable  
22 catalysts are those which tend to provide high yields (i.e., greater than about  
23 20, and, more preferably, greater than about 30 percent by weight of the  
24 products other than methane) of light ( $C_{2-8}$ ) alpha olefins.

25  
26 Preferably, the catalyst used in the first stage is an iron-containing catalyst.  
27 Iron itself can be used and, when iron oxides are formed, can be reduced with  
28 hydrogen back to iron. However, because the presence of iron fines in the  
29 product stream is not preferred, and because iron oxides (rust) decrease the  
30 surface area of the catalyst available for reaction, other iron-containing  
31 catalysts may be preferred. Examples of suitable iron-containing catalysts

1 include those described in U.S. Patent No. 4,544,674 to Fiato et al. and Xu  
2 et al., pp. 47-53, *Chemtech* (Jan. 1998).

3

4 In a preferred embodiment, the iron catalysts include at least about 10 to  
5 about 60 weight percent iron. More preferably, they include between about 20  
6 to about 60 weight percent iron, and most preferably about 30 to about  
7 50 weight percent iron. These catalysts can be unsupported, but are  
8 preferably promoted with a refractory metal oxide ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc.), alkali (K,  
9 Na, Rb) and/or Group IB metals (Cu, Ag). These catalysts are usually  
10 calcined, but usually are not reduced. Rather they are brought up to reaction  
11 temperature directly in the  $\text{CO}/\text{H}_2$  feed.

12

13 Co-precipitated iron-based catalysts, including those containing cobalt, can be  
14 used. High levels of cobalt in an iron-cobalt alloy are known to produce  
15 enhanced selectivity to olefinic products, as described, for example, in Stud.  
16 Surf. Sci. Catal. 7, Pt/A, p. 432 (1981).

17

18 Examples of co-precipitated iron-cobalt catalysts and/or alloys include those  
19 described in U.S. Patent Nos. 2,850,515, 2,686,195, 2,662,090, and  
20 2,735,862; *AIChE* 1981 Summer Nat'l Meeting Preprint No. 408, "The  
21 Synthesis of Light Hydrocarbons from CO and  $\text{H}_2$  Mixtures over Selected  
22 Metal Catalysts" ACS 173rd Symposium, Fuel Division, New Orleans, March  
23 1977; *J. Catalysis* 1981, No. 72(1), pp. 37-50; *Adv. Chem. Ser.* 1981, 194,  
24 573-88; *Physics Reports* (Section C of *Physics Letters*) 12 No. 5 (1974)  
25 pp. 335-374; UK patent application No. 2050859A; *J. Catalysis* 72, 95-110  
26 (1981); *Gmelins Handbuch der Anorganische Chemie* 8, Auflage (1959),  
27 pg. 59; *Hydrocarbon Processing*, May 1983, pp. 88-96; and *Chem. Ing. Tech.*  
28 49 (1977) No. 6, pp. 463-468.

29

30 Methods for producing high surface area metal oxides are described, for  
31 example, in the French article, "C. R. Acad. Sc. Paris", p. 268 (28 May 1969)  
32 by P. Courte and B. Delmon. Metal oxides with a high surface area are

1 prepared by evaporating to dryness aqueous solutions of the corresponding  
2 glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was  
3 prepared was  $\text{CoFe}_2\text{O}_4$ .

4  
5 Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic  
6 ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction  
7 and carbiding (see, for example, U.S. Patent No. 4,544,674 to Fiato et al.).  
8 These catalysts tend to exhibit high activity and selectivity for  $\text{C}_2\text{-C}_6$  olefins  
9 and low methane production.

10  
11 The contents of each of the patents and publications referred to above is  
12 hereby incorporated by reference.

13  
14 Catalysts with high chain growth probabilities

15  
16 For the second stage of the Fischer-Tropsch chemistry, any catalyst that  
17 provides relatively high chain growth probabilities can be used. Preferably,  
18 the catalyst used in the second stage is a cobalt-containing catalyst.  
19 Ruthenium is also an effective Fischer-Tropsch catalyst, but is more  
20 expensive.

21  
22 One suitable cobalt catalyst that can be used is described in U.S. Patent  
23 No. 4,579,986, as satisfying the relationship:

24  
25 
$$(3 + 4R) > L/S > (0.3 + 0.4R),$$

26  
27 wherein:

28  
29  $L$  = the total quantity of cobalt present on the catalyst, expressed as  
30 mg Co/ml catalyst;

31  $S$  = the surface area of the catalyst, expressed as  $\text{m}^2/\text{ml}$  catalyst; and

1 R = the weight ratio of the quantity of cobalt deposited on the catalyst  
2 by kneading to the total quantity of cobalt present on the catalyst.

4 Other suitable catalysts include those described in U.S. Patent  
5 Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320.  
6 U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture  
7 of CoO, Al<sub>2</sub>O<sub>3</sub> and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the  
8 oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal  
9 oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth  
10 metal, with Mo-K on carbon being preferred.

12 U.S. Patent No. 4,088,671 discloses minimizing methane production by using  
13 a small amount of ruthenium on a cobalt catalyst. Supported ruthenium  
14 catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are  
15 disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.

17 In general, the amount of cobalt present in the catalyst is between about 1  
18 and about 50 weight percent of the total catalyst composition, more preferably  
19 between about 10.0 and 25 weight percent.

21 Preferably, the catalyst contains between about 3 and 60 ppw cobalt, between  
22 0.1 and 100 ppw of at least one of zirconium, titanium or chromium per  
23 100 ppw of support (typically, silica, alumina, or silica-alumina and mixtures  
24 thereof).

## Catalyst Supports

28 The type of support used can influence methane production. Suitable metal  
29 oxide supports or matrices which can be used to minimize methane  
30 production include alumina, titania, silica, magnesium oxide, alkaline earth  
31 titanates, alkali titanates, rare earth titanates and mixtures thereof.

1 Methane production can be decreased using supported ruthenium catalysts.  
2 Titania or titania-containing supports provide lower methane production than,  
3 for example, silica, alumina or manganese oxide supports. Accordingly,  
4 titania and titania-containing supports are preferred.

5  
6 Typically, the catalysts have a particle size of between 10 and 110 microns,  
7 preferably between 20 and 80 microns, more preferably between 25 and  
8 65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably  
9 between 0.3 and 0.75 g/cc. The catalysts typically include one or more of the  
10 above-mentioned catalytic metals, preferably including iron in the first stage  
11 and cobalt in the second stage, on one of the above-mentioned catalyst  
12 supports. Preferably, the cobalt-containing catalysts include about 10 to  
13 14 percent cobalt on a low density fluid support, for example, alumina, silica  
14 and the like, having a density within the ranges set forth above for the  
15 catalyst.

#### 16 17 Promoters and Noble Metals

18  
19 Methane selectivity is also influenced by the choice of promoter. Alkali metal  
20 promoters are known for reducing the methane selectivities of iron catalysts.  
21 Noble metals, such as ruthenium, supported on inorganic refractory oxide  
22 supports, exhibit superior hydrocarbon synthesis characteristics with relatively  
23 low methane production. Where a noble metal is used, platinum and  
24 palladium are generally preferred. Accordingly, alkali metal promoters and/or  
25 noble metals can be included in the catalyst bed of the first stage provided  
26 that they do not significantly alter the reaction kinetics from slow chain growth  
27 probabilities to fast chain growth probabilities.

#### 28 29 Manganese Salts

30  
31 The tendency for olefins to be readily hydrogenated on the cobalt catalyst  
32 tends to minimize the overall yield of C<sub>5</sub>+ products. The presence of



1 manganese and manganese salts in the catalyst and/or support tends to  
2 decrease the rate of olefin hydrogenation, and, for this reason, is preferred.  
3 Examples of suitable manganese-containing materials that can be used  
4 include manganese-containing zeolites, unsupported and alumina-supported  
5 manganese oxide catalysts, manganese molybdate. Examples of manganese  
6 oxide-containing catalysts and/or supports include  $\text{MnO}$ ,  $\text{Al}_2\text{O}_3\text{-MnO}$ ,  
7  $\text{SiO}_2\text{-MnO}$ ,  $\text{MnO-carbon}$ , Group IVB-manganese oxides, Group VB-  
8 manganese oxides, Group IA (alkali metal)-manganese oxides, Group IIA  
9 (alkaline earth metal)-manganese oxides and rare earth-manganese oxides  
10 and mixtures thereof. The preferred support is manganese oxide.

11  
12 Suitable manganese-containing catalysts are described, for example, in U.S.  
13 Patent Nos. 4,206,134 and 5,162,284. When these catalysts are used in  
14 Fischer-Tropsch chemistry under certain conditions, Cu-promoted  $\text{Co}_2\text{MnO}_4$   
15 showed an increased olefin content in the products versus Cu-promoted  
16  $\text{Co}_3\text{O}_4$ . U.S. Patent No. 4,206,134 discloses using MnO-supported Ru  
17 catalysts which also show this effect. U.S. Patent No. 4,624,968 discloses  
18 using an iron/manganese/potassium catalyst in Fischer-Tropsch synthesis.  
19 These catalysts are suitable for use in the first stage Fischer-Tropsch  
20 reaction.

21  
22 Catalysts in spinel form have been formed which include cobalt and  
23 manganese, in particular, copper-promoted cobalt-manganese spinels with  
24 the formula  $\text{Co}_{3-x}\text{MnO}_4$  where x is from about 0.5 to about 1.2, preferably  
25 from about 0.7 to about 1.0, most preferably about 1.0. The ratio of cobalt to  
26 manganese in the spinel is between about 1.5:1 and about 5:1. The amount  
27 of copper promoter in the composition is preferably from about 0.1 to about  
28 5 gram atom percent based on the total gram atoms of cobalt and manganese  
29 of the dry composition, more preferably from about 0.5 to about 2.0 weight  
30 percent. Copper-promoted cobalt-manganese catalysts appear to be  
31 significantly more active, and also better at minimizing olefin hydrogenation,

1 than analogs promoted with copper but not containing manganese, or  
2 catalysts containing manganese but not promoted with copper.

3

4 Ruthenium-containing catalysts can be used with manganese oxide, other  
5 manganese-containing oxides or mixtures of various manganese oxides as a  
6 catalyst support. These catalysts are suitable for use in the second stage  
7 Fischer-Tropsch reaction.

8

9 The disclosures of each of the patents and articles discussed above are  
10 incorporated herein by reference in their entirety.

11

#### 12 Synthesis Gas

13

14 Typically, the synthesis gas will contain hydrogen and carbon monoxide, and  
15 may include minor amounts of carbon dioxide and/or water. In the first stage,  
16 the ratio of hydrogen/carbon monoxide is between about 0.5 and 1.0,  
17 preferably around 0.5. In the second stage, the ratio of hydrogen/carbon  
18 monoxide is preferably greater than 1.0, more preferably between about 1.0  
19 and 2.0, still more preferably between about 1.0 and 1.5. A hydrogen/carbon  
20 monoxide ratio of 1.0 or less results in the formation of a relatively large  
21 proportion of oxygenated products, and for this reason, should be avoided.  
22 Ratios above about 1.5 tend to hydrogenate a relatively large portion of the  
23 olefins in the second stage before they can participate in chain growth  
24 reactions. Although the amount of hydrogen tends to increase in the first  
25 stage as carbon monoxide is consumed, additional hydrogen can be added to  
26 achieve a desired ratio. The syngas feed in the second stage can be adjusted  
27 to provide suitable ratios of hydrogen to carbon monoxide. The syngas feed  
28 in the second stage is also preferably adjusted to give a ratio of olefins/CO of  
29 between about 0.05 and 0.5 by weight. Below ratios of about 0.05, there  
30 tends to be not enough olefin to get a significantly useful effect.

31

### Operating Conditions

1  
2  
3 The first stage of the Fischer-Tropsch reaction is typically conducted at  
4 temperatures between about 270°C and 280°C, at a pressure of between  
5 about 1 and 20 ATM, in a slurry reactor or a fluidized bed reactor. Typical  
6 synthesis gas linear velocity ranges in the reactor are between about 2 and  
7 40 cm per sec., preferably between about 6 and 10 cm per sec. After the first  
8 stage, the mixture is preferably cooled to less than 100°C, more preferably  
9 below about 80°C, and still more preferably below about 70°C. When the  
10 mixture is cooled, water and optionally a C<sub>5</sub>+ fraction can be removed.  
11  
12 The resulting reaction mixture includes C<sub>2-4</sub> olefins and paraffins, C<sub>5</sub>+  
13 products, and about 40% by weight syngas. The products in the C<sub>2-4</sub> range  
14 are typically present in a ratio of about 75% olefins/25% paraffins by weight.  
15 The product mixture also tends to include water and about 5% carbon dioxide  
16 and 5% methane by weight. The reaction mixture is then added to the second  
17 stage Fischer-Tropsch reactor with additional syngas.  
18  
19 The second stage of the Fischer-Tropsch reaction is typically conducted in  
20 either a fixed bed reactor or a slurry reactor, where slurry reactors are  
21 preferred. The operating temperature of the fixed bed reactor is between  
22 about 200°C and 225°C, and the operating temperature of the slurry reactor is  
23 between about 225°C and 250°C, with a temperature around 240°C preferred.  
24 Typical synthesis gas linear velocity ranges in the reactor are from about 2 to  
25 40 cm per sec., preferably from about 6 to 10 cm per sec. The pressure is  
26 preferably between about 1 and 30 ATM, with pressures between 20 and  
27 30 ATM being particularly preferred. Above about 30 ATM, carbonyls may be  
28 formed and, therefore, pressures significantly about 30 ATM are not preferred.  
29 Further, the rate of reaction tends to increase with increased pressure, but  
30 tends to level off due to hydrodynamic problems at around 30 ATM.

31

1 The catalyst space velocities are typically between about 100 and  
2 10,000 cc/g/h, preferably between about 300 and 3,000 cc/g/h, for both  
3 stages.

4  
5 Following the second stage, the reaction mixture is preferably cooled to less  
6 than 100°C, and liquid products are trapped. Methane is preferably bled off to  
7 a syngas generator and recycled. Water is preferably removed.

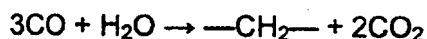
8  
9 As discussed above, slurry reactors can be preferred for one or both of the  
10 stages. Bubble column slurry reactors can be particularly preferred. Details  
11 regarding bubble column slurry reactors can be found, for example, in Y. T.  
12 Shah et al., Design Parameters Estimations for Bubble Column Reactors,  
13 *AIChE Journal*, 28 No. 3 pp. 353-379 (May 1982); Ramachandran et al.,  
14 Bubble Column Slurry Reactor, Three-Phase Catalytic Reactors Chapter 10,  
15 pp. 308-332 Gordon and Broch Science Publishers (1983); Deckwer et al.,  
16 Modeling the Fischer-Tropsch Synthesis in the Slurry Phase, Ind. Eng. Chem.  
17 Process Des. Dev. v 21, No. 2, pp. 231-241 (1982); Kölbel et al., The  
18 Fischer-Tropsch Synthesis in the Liquid Phase, Catal. Rev.-Sci. Eng., v.  
19 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982, the contents of  
20 each of which are hereby incorporated by reference in their entirety.

21  
22 Since the catalyst metal may be present in the catalyst in the form of an oxide,  
23 the catalyst may be reduced with hydrogen prior to contact with the slurry  
24 liquid. The starting slurry liquid is typically a heavy hydrocarbon that is  
25 viscous enough to keep the catalyst particles suspended (typically a viscosity  
26 between 4 and 100 centistokes at 100°C) and a low enough volatility to avoid  
27 vaporization during operation (typically an initial boiling point range of  
28 between about 350°C and 550°C). The slurry liquid is preferably essentially  
29 free of contaminants such as sulfur, phosphorous or chlorine compounds.  
30 Initially, it may be desirable to use a synthetic hydrocarbon fluid such as a  
31 synthetic olefin oligomer as the slurry fluid.

1 Often, a paraffin fraction of the product having the desired viscosity and  
2 volatility is recycled as the slurry liquid. The slurry typically has a catalyst  
3 concentration of between about 2 and 40 percent catalyst, preferably between  
4 about 5 and 20 percent, and more preferably between about 7 and 15 percent  
5 catalyst based on the total weight of the catalyst, i.e., metal plus support.

6  
7 Preferably, each reactor converts about 60% or more of the syngas to  
8 products, and the overall yield is preferably about 80% or greater, more  
9 preferably, about 90% or greater. In the first stage, above about 60%  
10 conversion, carbon dioxide production tends to increase, which is not  
11 preferred. The conversion in the second stage can go higher than about 60%.  
12 The product distribution tends to be about 50% hydrocarbons boiling in the  
13 diesel range, with up to 70% between C<sub>5</sub> and C<sub>20</sub>, and with about 15% or less  
14 in the C<sub>1-4</sub> range, and about 15% or less in the C<sub>20-50</sub> range.

15  
16 Although the stages described herein are described in terms of a  
17 Fischer-Tropsch reaction, these stages can optionally be performed using  
18 various modifications of the literal Fischer-Tropsch process where hydrogen  
19 (or water) and carbon monoxide (or carbon dioxide) are converted to  
20 hydrocarbons (e.g., paraffins, ethers, etc.). Thus, the term Fischer-Tropsch  
21 type product or process is intended to apply to Fischer-Tropsch processes  
22 and products and the various modifications thereof and the products thereof.  
23 For example, the term is intended to apply to the Kolbel-Engelhardt process  
24 typically described by the reaction:



27  
28 The CO<sub>2</sub> product can be returned to the syngas generator and combined with  
29 methane (and some air) to form additional syngas.

30

1        The Separation of Product From the Fischer-Tropsch Reaction

2

3        The products from Fischer-Tropsch reactions generally include a gaseous  
4        reaction product and a liquid reaction product. The gaseous reaction product  
5        includes hydrocarbons boiling below about 650°F (e.g., tail gases through  
6        middle distillates). The liquid reaction product (the condensate fraction)  
7        includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil  
8        through heavy paraffins).

9

10       The minus 650°F product can be separated into a tail gas fraction and a  
11       condensate fraction, i.e., about C<sub>5</sub> to C<sub>20</sub> normal paraffins and higher boiling  
12       hydrocarbons, using, for example, a high pressure and/or lower temperature  
13       vapor-liquid separator or low pressure separators or a combination of  
14       separators.

15

16       The fraction boiling above about 650°F (the condensate fraction) is typically  
17       separated into a wax fraction boiling in the range of about 650°F-1200°F after  
18       removing particulate catalyst fines and one or more fractions boiling above  
19       about 1200°F. The wax fraction primarily contains C<sub>20</sub> to C<sub>50</sub> linear paraffins  
20       with relatively small amounts of higher boiling branched paraffins. Typically,  
21       the separation is effected by fractional distillation.

22

23                    Optional Process Steps

24

25       The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic  
26       contaminants in the feedstock is undesirable. For this reason, it is preferred  
27       to remove sulfur and other contaminants from the feed before performing the  
28       Fischer-Tropsch chemistry. Means for removing these contaminants are well  
29       known to those of skill in the art. For example, ZnO guardbeds are preferred  
30       for removing sulfur impurities. Means for removing other contaminants are  
31       well known to those of skill in the art.

1 In one embodiment, any methane produced by the reaction is recovered and  
2 converted to synthesis gas for recycling in the process. Alternatively, the  
3 entire product stream from the first reactor can be added to the second  
4 reactor.

5  
6 In some embodiments, the product stream from the second stage may contain  
7 a relatively large amount of olefins that can be hydrogenated following the  
8 Fischer-Tropsch chemistry. Optionally, these olefins can be isomerized prior  
9 to hydrogenation to provide branched paraffins. Branching may be  
10 advantageous in a number of end-uses, particularly when increased octane  
11 values (when the compositions are used as fuels) or decreased pour points  
12 are desired.

13  
14 After the reaction mixture is converted to the final product stream, the desired  
15 products can be isolated, for example, by distillation.  $C_{1-4}$  products can be  
16 obtained and used to form synthesis gas for subsequent use in the process  
17 described herein.  $C_{5-12}$  products can be isolated and used, for example, as  
18 combustible fuels.

19  
20 Higher molecular weight products can either be isolated and used directly, or  
21 can be reacted to form lower molecular weight products, as desired. For  
22 example, high molecular weight products can be hydrocracked to provide  
23 lower molecular weight products, increasing the yield of liquid combustible  
24 fuels.

25  
26 Hydrocracking refers to a catalytic process, usually carried out in the  
27 presence of free hydrogen, in which the cracking of the larger hydrocarbon  
28 molecules is a primary purpose of the operation. Desulfurization and/or  
29 denitrification of the feed stock usually will also occur.

30  
31 Catalysts used in carrying out hydrocracking operations are well known in the  
32 art, and it should not be necessary to describe them in detail here. See, for

1 example, U.S. Patent Nos. 4,347,121 and 4,810,357 for general descriptions  
2 of hydrotreating, hydrocracking, and typical catalysts used in each process.  
3 The product from the hydrocracking can be subject to distillation and/or  
4 catalytic isomerization to provide lube oils, diesel fuel, and the like.

5  
6 Optionally, an acid catalyst can be added to the reaction mixture in either  
7 stage, but preferably in the second stage. When  $C_4+$  alpha-olefins are  
8 produced, the alpha-olefins isomerize to more substituted olefins in the  
9 presence of the acid catalyst. This reduces the chain growth probability for  
10  $C_4+$  and largely minimizes wax formation.

11  
12 The process will be readily understood by referring to the flow diagram in  
13 Figure 4. In Figure 4, a mixture of carbon monoxide and hydrogen (syngas) is  
14 added to a first stage Fischer-Tropsch reactor (Box 10). The products are  
15 cooled, water is removed and the  $C_5+$  fraction is isolated via distillation (Box  
16 40) and contained in Box 20. The  $C_{1-4}$  fraction and additional syngas is sent  
17 to a second stage Fischer-Tropsch reactor (Box 30). The product of the  
18 reaction is fractionally distilled (Box 40). The  $C_{1-4}$  fraction is sent to a syngas  
19 generator (Box 50). The  $C_{5-20}$  fraction is collected (Box 20) separately from  
20 the  $C_{20+}$  fraction, which is optionally hydrocracked and/or hydrotreated  
21 (Box 60). In the flow scheme contained in Figure 4, the process of the  
22 present invention is practiced in continuous operation. However, it is possible  
23 to practice the present invention in batch operation.

24 The following example will help to further illustrate the invention but are not  
25 intended to be a limitation on of the scope of the process.

26



Example 1

Addition of ethylene to a Cobalt-Catalyzed Fischer-Tropsch Reaction

EXPERIMENTAL

CRLA -2B Catalyst

The catalyst had a nominal composition of 20 wt. % Co, 0.5 wt. % Ru, 1 wt. %  $\text{La}_2\text{O}_3$ , and 78.5 wt. %  $\text{Al}_2\text{O}_3$ . It was prepared from a Ketjen fluid alumina by suspending the alumina in a hot (80°C) aqueous solution of the nitrate salts of Co, Ru, and La (nitrosyl nitrate for Ru). A hot aqueous solution of potassium carbonate was added to the suspended alumina with vigorous stirring. The metals then precipitated onto the support as hydroxides. The solids were filtered and washed several times with hot distilled water, then calcined in a fluid bed reactor by heating them slowly in air to 300°C. They were cooled to room temperature, then reduced by heating them slowly (1°C/min.) to 350°C in pure hydrogen at atmospheric pressure. The reducing gas flow equaled or exceeded 1800 cc/g/h. After cooling and purging with nitrogen, the reduced catalyst was passivated by adding enough dilute air at ambient temperature to reoxidize the metals completely, at a slow enough rate that the oxidation exotherm did not exceed 50°C. A hydrogen TPD test indicated that the Co dispersion of the catalyst was about 10%.

Tests with Pure Synthesis Gas

Tests of the fluid catalyst were made on 4-gram quantities of the fluid particles in a fixed bed reactor after they were diluted with an equal volume of 0.5 mm glass beads. The temperature control was within  $\pm 1^\circ\text{C}$  under all conditions. Activation was done in hydrogen at atmospheric pressure at a flow rate of 1800 cc/g/h. The heating rate was 1°C/min. to 350°C and the hold at that temperature was two hours. After activation, the catalyst was cooled in hydrogen to 185°C for the start of the synthesis run. Initial startup was at 185°C and 1 atm with a 900 cc/g/h flow of synthesis gas having  $\text{H}_2/\text{CO} = 1.5$ .

1 Those conditions were maintained for one hour before switching to the  
2 experimental conditions.

3

4 Tests with Synthesis Gas plus Ethylene and/or Water

5 Tests with added ethylene were made after the catalyst was started up in pure  
6 synthesis gas at 185°C and operated for at least one hour at that condition  
7 before it was heated to 200°C. During the tests, ethylene was added at either  
8 a 1:2 or 1:1 mole ratio with CO. Total flow rates were adjusted to 900 cc/g/h  
9 or 1800 cc/g/h. To examine the effects of added water on Fischer-Tropsch  
10 synthesis and olefin hydrogenation, inlet gases were passed through a  
11 saturator held at 22°C. This produced a reactant stream containing 2.6 vol. %  
12 water.

13

14 RESULTS

15 All experiments were run at 200°C and one atmosphere pressure.  
16 Compositions of the inlet streams and flow rates for each experiment are  
17 shown in Table 1 and Table 2.

Table 1. Synthesis Gas Conversion over CoRu-La<sub>2</sub>O<sub>3</sub>/Alumina

Temperature, °C	200	200	200	200	200	200	200	200
Pressure, atm	1	1	5	5	1	1	5	5
H <sub>2</sub> /CO Ratio	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0
CO GHSV, cc/g/h	720	360	720	360	720	360	720	360
H <sub>2</sub> GHSV, cc/g/h	1080	540	1080	540	1080	540	1080	540
CO Conversion, %	33.0	53.9	52.8	72.6	20.3	29.3	29.4	44.9
CO Rate, cc/g/h	238	194	380	261	183	132	265	202
H <sub>2</sub> Conversion, %	46.2	66.7	71.6	91.0	38.9	61.7	66.8	84.7
H <sub>2</sub> Rate, cc/g/h	499	360	773	491	350	278	601	381
Product Wt%								
H <sub>2</sub> O	46.9	42.7	49.7	38.0	48.4	52.5	52.0	48.1
CO <sub>2</sub>	16.4	20.0	9.2	23.6	7.7	9.0	5.8	11.7
CH <sub>4</sub>	9.3	8.0	8.4	8.3	6.4	6.0	5.3	4.5
C <sub>2</sub> -C <sub>4</sub>	10.6	10.2	7.2	6.3	8.7	8.3	6.2	5.0
C <sub>5</sub> +	16.8	19.2	25.6	23.9	28.8	24.1	30.7	30.7
H <sub>2</sub> O Rate, g/g/h	0.160	0.117	0.270	0.141	0.126	0.099	0.200	0.138
CO <sub>2</sub> Rate, g/g/h	0.056	0.055	0.050	0.087	0.020	0.017	0.022	0.034
CH <sub>4</sub> Rate, g/g/h	0.031	0.021	0.046	0.031	0.015	0.010	0.022	0.013
C <sub>2</sub> -C <sub>4</sub> Rate, g/g/h	0.035	0.027	0.039	0.024	0.020	0.014	0.026	0.014
C <sub>5</sub> +	0.056	0.050	0.141	0.088	0.069	0.042	0.125	0.090
Total HC Rate, g/g/h	0.122	0.098	0.226	0.143	0.104	0.066	0.173	0.117

Table 2. Synthesis Gas Conversion over CoRu-La<sub>2</sub>O<sub>3</sub>/Alumina

Temperature, °C	200	200	200	200	200	200	200	200	200
Pressure, atm	1	1	5	1	1	1	1	5	5
H <sub>2</sub> /CO Ratio	1.5	1.5	1.5	1.0	1.0	1.0	1.0	1.0	1.0
CO GHSV, cc/g/h	701	584	701	877	877	701	877	877	701
H <sub>2</sub> GHSV, cc/g/h	1052	877	1052	877	877	701	877	877	701
C <sub>2</sub> H <sub>4</sub> GHSV, cc/g/h	0	292	0	292	0	351	0	0	351
H <sub>2</sub> O GHSV, cc/g/h	47	47	47	47	47	47	47	47	47
CO Conversion, %	30	19	32	33	17	14	22	22	22
C <sub>2</sub> H <sub>4</sub> Conversion, %	...	67	...	75	...	51	...	...	67
C <sub>2</sub> H <sub>4</sub> to C <sub>3</sub> +, %	...	44	...	35	...	48	...	...	50
H <sub>2</sub> Conversion, %	45	39	46	62	35	40	67	67	69
Product Weight,									
H <sub>2</sub> O	50	28.9	46.9	40.1	41.4	29.8	45.9	45.9	33.4
CO <sub>2</sub>	11.2	5.3	5.6	6.3	23.9	11.6	4.7	4.7	4.4
CH <sub>4</sub>	9.5	6	7.7	4.9	7.6	4.3	5.5	5.5	3.2
C <sub>2</sub> -C <sub>4</sub>	11.2	23.2	8	10.4	10.3	22.1	6.4	6.4	11.1
C <sub>5</sub> +	18.2	36.5	31.8	38.3	16.9	32.3	37.5	37.5	48
Product Rates									
H <sub>2</sub> O Rate, g/g/h	0.132	0.058	0.152	0.147	0.100	0.075	0.117	0.117	0.115
CO <sub>2</sub> Rate, g/g/h	0.026	0.024	0.018	0.023	0.041	0.039	0.012	0.012	0.015
CH <sub>4</sub> Rate, g/g/h	0.016	0.012	0.025	0.018	0.019	0.011	0.014	0.014	0.011
		-0.004		-0.007		-0.008			-0.003

C <sub>2</sub> -C <sub>4</sub> Rate, g/g/h	0.022	0.045	0.026	0.038	0.023	0.058	0.016	0.038
C <sub>5</sub> + Rate, g/g/h	0.048	0.063	0.101	0.143	0.041	0.087	0.097	0.168
	+0.015			+0.042		+0.046		+0.071
Total CH <sub>x</sub> Rate, g/g/h	0.086	0.120	0.152	0.199	0.083	0.156	0.127	0.217
	+0.034			+0.047		+0.073		+0.080

- 1
- 2 For experiments with added ethylene, the C<sub>2</sub> fraction was excluded from the product analyses.

1    **Synthesis Gas Only**

2    Results at several flow rates over the fluid CoRu catalyst operating at one  
3    atmosphere and 200°C are shown in Table 1. Conversions were high for  
4    these runs, and the main change with flow rate was a change in the  
5    conversion level and in the amount of CO<sub>2</sub> that was produced. The CO  
6    conversion rate increased with increasing space velocity (see Figure 1) and  
7    the CO<sub>2</sub> formation rate increased almost linearly with increasing CO  
8    conversion.

9  
10   **Synthesis Gas Plus Ethylene**

11   Experiments with added ethylene were made at either 1 atm or 5 atm  
12   pressure, with or without saturation of the gas feed with water. The water had  
13   little effect other than to depress the CO conversion rate slightly. Data for  
14   runs with added water are shown in Table 2. The H<sub>2</sub>/CO ratio in the gas feed  
15   was either 1.0 or 1.5, while the amount of added ethylene was either zero or  
16   one-half the amount of CO (so that the number of moles of carbon in C<sub>2</sub>H<sub>4</sub>  
17   and CO were equal).

18  
19   In each case where ethylene was added, the hydrocarbon synthesis rate  
20   increased significantly and a large portion of the C<sub>3</sub>+ products were derived  
21   from ethylene. This was not accompanied by a corresponding increase in the  
22   methane formation rate. On the contrary, the formation rate for methane  
23   decreased when ethylene was added (see Table 2). This would be expected  
24   if the main function of ethylene is to initiate new hydrocarbon chains. In that  
25   case, the fraction of C<sub>1</sub> species at active sites would be expected to decrease  
26   as the fraction of C<sub>2</sub> species increases.

27  
28   At one atmosphere pressure, the CO conversion rate declined when ethylene  
29   was added, but at five atmospheres pressure it was relatively unaffected by  
30   ethylene addition. Also, the increase in hydrocarbon synthesis rate was  
31   concentrated mainly in the C<sub>5</sub>+ fraction at 5 atm pressure, while at 1 atm

1 pressure much of the increase was in C<sub>3</sub> and C<sub>4</sub> products. These effects are  
2 shown in Figure 2 and Figure 3.

3

4 The increase in C<sub>5</sub>+ synthesis rates with ethylene addition was much more  
5 pronounced at H<sub>2</sub>/CO = 1 than at H<sub>2</sub>/CO = 1.5 (see Table 2, Figure 2 and  
6 Figure 3). Also, the fraction of ethylene incorporated into C<sub>3</sub>+ products was  
7 greater at that ratio. Thus, the best results for ethylene incorporation into  
8 liquid hydrocarbons in these tests were obtained at 5 atm pressure and  
9 H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/CO = 1:0.5:1.

10

11 Lower H<sub>2</sub>/CO ratios would appear to favor better utilization of added ethylene  
12 (less hydrogenation to ethane), but may also cause excessive CO<sub>2</sub> production  
13 at higher conversion levels or else limit the conversion, since the usage ratio  
14 is two H<sub>2</sub> molecules per CO molecule. The H<sub>2</sub>/CO ratio in the reactor will drop  
15 with increasing conversion, lowering the conversion rate, unless it is  
16 replenished by the water gas shift reaction:  $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2$ . It is  
17 believed that a ratio of H<sub>2</sub>/CO of 1.0 is the lowest ratio that should be used.

1 WHAT IS CLAIMED IS:

2

3 1. An integrated process for preparing liquid fuels, the process comprising:

4

5 (a) subjecting syngas with a hydrogen/carbon monoxide ratio of  
6 between about 0.5 and 1.0 to Fischer-Tropsch reaction conditions  
7 where the catalyst used for the Fischer-Tropsch reaction is one  
8 which provides low to moderate chain growth probabilities;

9

10 (b) optionally removing water and/or C<sub>5</sub>+ hydrocarbons from the  
11 product stream;

12

13 (c) subjecting the product from step (a) or (b) to Fischer-Tropsch  
14 reaction conditions where the catalyst used for the Fischer-Tropsch  
15 reaction is one which provides high chain growth probabilities,  
16 where the hydrogen/carbon monoxide ratio is between about 1.0  
17 and 2.0; and

18

19 (d) isolating the product of the reaction.

20

21 2. The process of claim 1, wherein the catalyst with low to moderate chain  
22 growth probabilities is an iron-containing catalyst.

23

24 3. The process of claim 1, wherein the catalyst with high chain growth  
25 probabilities is a cobalt-containing catalyst.

26

27 4. The process of claim 1, wherein step a) is conducted at a temperature  
28 between about 270°C and 280°C and at a pressure of between about 1  
29 and 20 ATM.

30



- 1    5.    The process of claim 1, wherein step (a) is conducted in a slurry reactor  
2        or a fluidized bed reactor.
- 3    6.    The process of claim 1, wherein the product stream is cooled to less  
4        than 100°C and at least a portion of the water produced during the  
5        reaction is removed.  
6
- 7    7.    The process of claim 1, wherein a C<sub>5</sub>+ fraction is isolated after step (a)  
8        and before step (c).  
9
- 10   8.    The process of claim 1, wherein at least a portion of the olefins prepared  
11        in step (a) are isomerized before being subjected to the Fischer-Tropsch  
12        reaction conditions in step (c).  
13
- 14   9.    The process of claim 1, wherein step (c) is conducted at a temperature  
15        between about 200°C and 250°C and at a pressure between about 1  
16        and 30 ATM.  
17
- 18   10.   The process of claim 1, wherein the product of step (a) in the C<sub>2-4</sub> range  
19        includes about 75% olefins by weight.  
20
- 21   11.   The process of claim 1, wherein the Fischer-Tropsch reactions in steps  
22        (a) and/or (c) are run in a slurry reactor.  
23
- 24   12.   The process of claim 1, wherein olefin hydrogenation in steps (a) and/or  
25        (c) is minimized by adding a manganese-containing compound to the  
26        reaction.  
27
- 28   13.   The process of claim 1, wherein the hydrogen/carbon monoxide ratio in  
29        step (c) is between about 1.0 and 1.5.  
30
- 31   14.   The process of claim 1, wherein unreacted syngas is recycled.

15. The process of claim 14, wherein a at least a portion of the carbon dioxide is removed from the syngas before it is recycled.

5 16. An integrated process for preparing liquid fuels, substantially as described and shown in Figure 4 of the accompanying drawings.

17. A hydrocarbon product produced by the process of any preceding claim.

10



INVESTOR IN PEOPLE

Application No: GB 0104292.8  
Claims searched: 1-17

Examiner: Dr William Thomson  
Date of search: 17 May 2001

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C5G (GAD)

Int Cl (Ed.7): C10G 2/00

Other: ONLINE: CAS-ONLINE, EPODOC, JAPIO, WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	US 4624968 (KIM ET AL) See whole document, in particular column 3, lines 17-49, the Example and claims 1-4	1, 2, 4, 5, 9, 12 and 13
X	Chemical Abstract No 131:353528 & CN 1137058 (B.ZHONG ET AL), 01/12/96 See abstract	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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